

# Precision Cleaning of Semiconductor Surfaces Using Carbon Dioxide-Based Fluids

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## Biography

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## Abstract:

The Los Alamos National Laboratory, on behalf of the Hewlett-Packard Company, is conducting tests of a closed-loop CO<sub>2</sub>-based supercritical fluid process, known as **Supercritical CO<sub>2</sub> Resist Remover (SCORR)**. We have shown that this treatment process is effective in removing hard-baked, ion-implanted photoresists, and appears to be fully compatible with metallization systems. We are now performing experiments on production wafers to assess not only photoresist removal, but also residual surface

contamination due to particulates and trace metals.

Dense-phase (liquid or supercritical)  $\text{CO}_2$ , since it is non-polar, *acts like* an organic solvent and therefore has an inherently high solubility for organic compounds such as oils and greases. Also, dense  $\text{CO}_2$  has a low-viscosity and a low dielectric constant. Finally,  $\text{CO}_2$  in the liquid and supercritical fluid states can solubilize metal complexing agents and surfactants. This combination of properties has interesting implications for the removal not only of organic films, but also trace metals and inorganic particulates. In this paper we discuss the possibility of using  $\text{CO}_2$  as a precision-cleaning solvent, with particular emphasis on semiconductor surfaces.

**Data:**

Aqueous-based solutions currently used for wafer cleaning generate large waste streams, and the inherently high surface tension of these solutions limits their use in cleaning substrates containing very-fine-scale structures. Surfactants can be used to reduce surface tension, but this necessitates a subsequent rinsing and drying step, requiring additional amounts of ultrapure water. Also, the withdrawal of wafers through the liquid/gas boundary following the clean invariably leads to re-deposition of particulates.

One of the processes being evaluated for advanced IC manufacturing is dry (vapor-phase) cleaning, to replace traditional aqueous-based immersion cleaning.[1] As an extension of current work on photoresist stripping, performed at Los Alamos on behalf of the Hewlett-Packard Company, we are investigating the possibility of using carbon dioxide ( $\text{CO}_2$ ), either as a liquid or a supercritical fluid, as a precision cleaning solvent.

The temperature at which the vapor pressure above a pure liquid reaches one atmosphere is known as the normal boiling point. The normal boiling point of liquid water, at one atmosphere, is  $100^\circ\text{C}$ . In an open container, Figure 1, the temperature of liquid water cannot be raised above  $100^\circ\text{C}$  since this would cause the vapor pressure of the water to rise above one atmosphere,

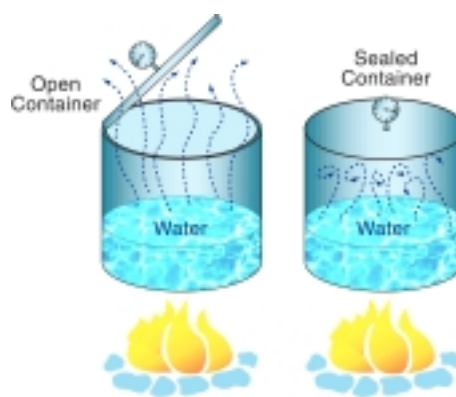


Figure 1. Formation of a supercritical fluid by heating of a liquid in a sealed container.

exceeding the ambient pressure. If we place a quantity of water in a sealed container, however, then we may heat the liquid water to higher temperatures, since the vapor pressure of the water can increase beyond one atmosphere. As we uniformly heat the sealed container, the density of the liquid water decreases through thermal expansion. Simultaneously, the density of the water vapor increases. We can continue this heating process until, eventually, the density of the liquid becomes so reduced, and the density of the vapor phase is so increased, that the two densities become equal. The temperature at which the liquid and vapor densities become equal is called the critical temperature. Since the temperature inside the sealed container is everywhere equal, and the density is

everywhere equal, thermodynamics dictates that the pressure inside the container be everywhere equal. This pressure is called the critical pressure. A fluid which has been brought to conditions above its critical temperature and pressure is known as a supercritical fluid. This physical description of the critical temperature and pressure suggests that all simple liquids (and gases) can be made into a supercritical fluid by generating the appropriate conditions of temperature and pressure. This is indeed correct, and Table 1 gives the critical temperature and pressure of some common fluids.

Supercritical fluids are used as solvents in many commercial applications, including the extraction of caffeine from coffee and essential oils and spices from plants for use in perfumes and foods. The attractiveness of supercritical fluids as solvents stems from their unique combination of liquid-like and gas-like properties. Table 2 gives a comparison of the diffusivity, viscosity and density of a typical organic fluid in the liquid, gas, and supercritical fluid state.

To a first approximation, the solvent power of a fluid is related to its density. The high, liquid-like densities achievable in supercritical fluids therefore allows for substantial solubilities. Figure 2 shows the pressure-temperature-density surface for pure CO<sub>2</sub>. The critical point for pure CO<sub>2</sub>,  $T_c = 31^\circ\text{C}$  and  $P_c = 1072$  psi ( $\approx 73$  atmospheres), is

*Table 1. Critical temperature,  $T_c$ , and pressure,  $P_c$ , for some common fluids.*

Fluid	$T_c$ ( $^\circ\text{C}$ )	$P_c$ (psi)
Neon, Ne	-229	400
Nitrogen, N <sub>2</sub>	-147	492
Argon, Ar	-122	706
Xenon, Xe	17	858
carbon dioxide, CO <sub>2</sub>	31	1072
sulfur hexafluoride, SF <sub>6</sub>	46	545
propane, C <sub>3</sub> H <sub>8</sub>	97	617
ammonia, NH <sub>3</sub>	133	1654
water, H <sub>2</sub> O	374	3209

*Table 2. Comparison of physico-chemical properties of a typical organic fluid in the liquid, gas, and supercritical fluid state.*

	Diffusivity (cm <sup>2</sup> /s)	Viscosity (cP) or (mN·s/m <sup>2</sup> )	Density (kg/m <sup>3</sup> )
Liquid	10 <sup>-5</sup>	1	1000
Supercritical fluid	10 <sup>-3</sup>	10 <sup>-2</sup>	300
Gas	10 <sup>-1</sup>	10 <sup>-2</sup>	1

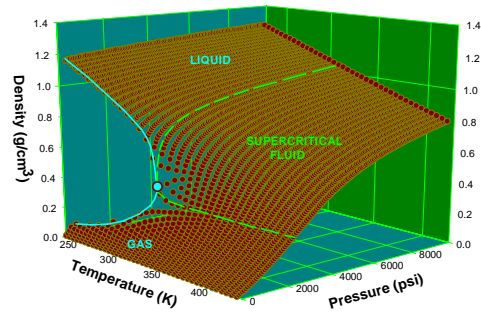
shown in Figure 2 by the large solid circle. It can be seen that relatively small changes in temperature or pressure, near the critical point, result in large changes in density. It is this tunability of density, and therefore tunability of solvent power, which is one of the most attractive attributes of supercritical fluids. Also, the gas-like properties of low viscosity and high diffusivity provides for effective penetration into very fine scale structures such as high aspect ratio vias and through holes. Finally, the absence of surface tension provides for excellent wettability.

There has been considerable progress in developing supercritical fluids, and supercritical CO<sub>2</sub> (SCCO<sub>2</sub>) in particular, for the precision-cleaning of inorganic surfaces,[2,3,4] including metals,[5,6,7,8] glass,[9,10] optical elements,[11] and one report on its applicability to Si wafers.[12]

One advantage of CO<sub>2</sub> for precision cleaning is that the process leaves no residues, since it evaporates completely when

depressurized. As a result, subsequent aqueous rinsing and drying steps are not required. There is a commercial system available for SCCO<sub>2</sub> cleaning of micro-electromechanical device fabrication,[13] and is becoming a popular processing technique.[14,15,16,17].

Another advantage to using CO<sub>2</sub> for surface cleaning is its inertness with respect to inorganic materials. Aluminum films exposed to dry CO<sub>2</sub> gas showed low rates of adsorption and little or no chemical reaction.[18] Pure, dry supercritical CO<sub>2</sub> has been shown to have no



*Figure 2. Pressure-temperature-density surface of pure CO<sub>2</sub>.*

corrosive action on stainless steel,[19] iron,[20] or copper.[21,22,23] It is known from geochemical studies that there is a vanishingly small solubility for  $\text{SiO}_2$  in  $\text{CO}_2$ . [24,25] Also, Khemka and Chow [26] found that an oxidation anneal of Si in pure  $\text{CO}_2$  at 1000 and 1100°C produced an oxide thickness of only 10 nm, independent of annealing time. A thermodynamic analysis of possible reactions between  $\text{CO}_2$  and  $\text{Si}_3\text{N}_4$  [27] shows that, at the temperatures and pressures of semiconductor processing, no reaction between these compounds is expected. Finally, it has been shown that surface-adsorbed  $\text{CO}_2$  does not dissociate or chemically react with a highly active, hydroxylated  $\text{SiO}_2$  surface.[28]

In this paper, we examine the potential of liquid and supercritical fluid  $\text{CO}_2$  for removing organic films, trace metals and particulates from Si wafers. We accomplish this by comparing how immersion in liquid and supercritical  $\text{CO}_2$  would behave, relative to immersion in pure water.

### ***1. Organic surface films***

$\text{SCCO}_2$  is an excellent solvent for nonpolar, low molecular-

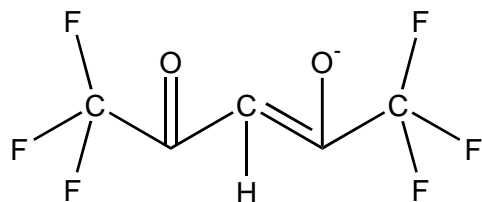
weight organic compounds, such as greases, oils, lubricants and fingerprints.[29,30] It is this ability to solubilize organic compounds which underlies the commercial applications mentioned previously. Extensive compilations of the solubility of organics in liquid  $\text{CO}_2$  can be found in [31], while compilations for supercritical  $\text{CO}_2$  can be found in [32].

### ***2. Trace Metals***

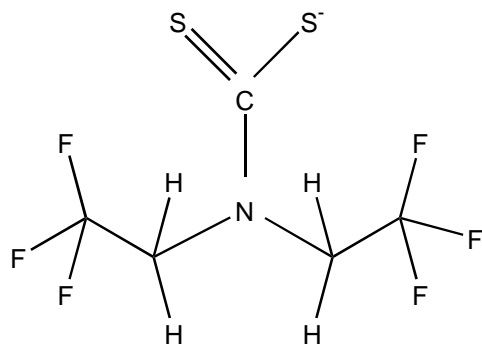
Current aqueous immersion cleaning removes metallic contaminants by the formation of soluble metal complexes. For example,  $\text{HCl}/\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  solutions are effective at removing Cu by forming soluble chloride and sulfate complexes, respectively.[33] In a similar manner, a reactive component, dissolved in a supercritical fluid, can be used to remove trace metal contaminants either by surface etching of Si and  $\text{SiO}_2$ , or by selective chelation. The potential advantage of using  $\text{SCCO}_2$  to “scavenge” these metals is an enhanced removal rate resulting from the low viscosity and high diffusivity.

By definition, compounds which are gaseous at the conditions of temperature and pressure of SCCO<sub>2</sub> will be soluble. Therefore, compounds such as SF<sub>6</sub>, BF<sub>3</sub>, and C<sub>2</sub>F<sub>6</sub>, which are gaseous at SCCO<sub>2</sub> conditions, will be soluble in SCCO<sub>2</sub>. For the case of liquids and solids, the situation is only slightly more complex. While it is well known that dense CO<sub>2</sub> is capable of solubilizing low molecular weight organic compounds, it is also true that CO<sub>2</sub> can solubilize inorganic compounds *if they act like organic compounds*, in terms of (a) low molecular weight (b) nonpolarity, and (c) existing as discrete molecular species. For example, TiCl<sub>4</sub> [34] and SnCl<sub>4</sub> [35,36] have been shown to be very soluble in supercritical CO<sub>2</sub>. As an example of a potential application, Sugino *et al.* [37] used a dry Cl<sub>2</sub> + SiCl<sub>4</sub> mixture to remove Fe contamination from Si and SiO<sub>2</sub> surfaces. Both of these compounds are soluble in dense CO<sub>2</sub>. George *et al.* [38] has shown that a CVD precursor compound, called a  $\beta$ -diketonate and shown in Figure 3a, dissolved in a flowing N<sub>2</sub> stream, can scavenge Cu from Si surfaces. Ueno *et al.* [39] used this same compound, dissolved in a flowing argon stream, to remove Cu<sub>2</sub>O and CuO from SiO<sub>2</sub> and Cu surfaces. Also, Pearton *et al.* [40] used this compound, dissolved in N<sub>2</sub>, to

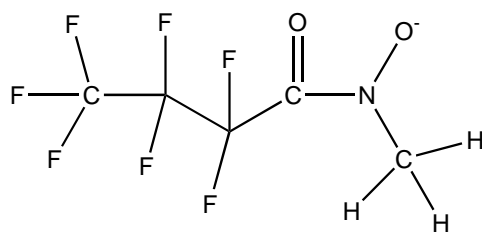
remove metallic ions from dry-etched AlGaAs at elevated temperature.  $\beta$ -diketonate compounds have been shown to be effective chelators in SCCO<sub>2</sub>. [41,42,43,44,45,46,47,48,49,



a) 1,1,1,5,5,5-hexafluoro-2,4-pentanedione.



b) bis(trifluoroethyl)dithiocarbamate).



c) n-methylheptafluorobutyrylhydroxamic acid.

Figure 3. Structures of some chelating compounds used for chelation/extraction of metals in supercritical CO<sub>2</sub>.

50] Finally, a compound closely related to the  $\beta$ -diketonates, trifluoroacetic anhydride (TFAA), is being evaluated for PECVD chamber cleaning.[51] A similar approach can be used with dense-phase  $\text{CO}_2$  as the carrier stream. The solubilities and behavior of several metal/chelate systems, in addition to  $\beta$ -diketonates, have been investigated in supercritical  $\text{CO}_2$ , including crown ethers,[52] dithiocarbamates (Figure 3b) [53,54,55,56,57,58,59,60] amines,[61] hydroxamic acids (Figure 3c),[62] and organophosphates.[63,64,65]

### 3. Particulates

#### 3.1. Mechanics of Particle Removal

To evaluate the ability of liquid and supercritical  $\text{CO}_2$ , to remove particulates, we estimate the magnitude of various adhesion forces acting between a perfectly smooth, spherical  $\text{SiO}_2$  particle and a perfectly smooth, flat Si surface immersed in liquid  $\text{CO}_2$ , supercritical  $\text{CO}_2$  and water. We choose  $\text{SiO}_2$  as representative of the particles which are largely insoluble in aqueous acidic and alkaline cleaning solutions.

There are a number of adhesion forces that can act between a particle and a surface, including chemical bonding. In this discussion, however, we will neglect such

chemical bonding forces, as these are not well enough understood to allow even approximate calculation. Also, we neglect diffusive mixing, surface diffusion and other less-commonly-encountered adhesion mechanisms.

Figure 4 shows the types of long-range attractive forces between a particle and a surface. We will assume that the particle is non-magnetic. In addition to the forces shown in Figure 4, we will also consider the magnitude of the gravitational force holding the particle onto the (horizontal) substrate and the capillary forces which exist in humid environments.

#### A. van der Waals Force

There are several components to the van der Waals force between a particle and a surface. There is a component due to (i) interaction between permanent dipoles (van der Waals-Keesom force), (ii) interaction between permanent dipoles and induced dipoles (van der Waals-Debye force), and (iii) interaction between induced

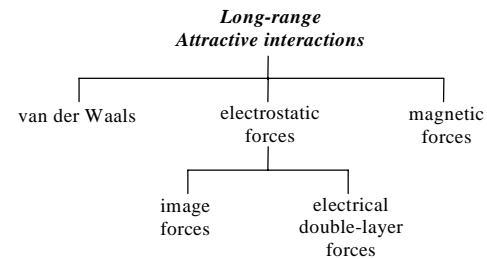


Figure 4. Long-range attractive forces acting between a particle and a surface.[66]

dipoles (van der Waals-London force).[67] The one of greatest importance here is the van der Waals-London force. This is an attractive force that arises due to instantaneous fluctuations of molecular dipoles, and occurs in all substances.

For the case of a spherical particle of material 1, a planar substrate of material 2, both immersed in a medium 3, the van der Waals-London force,  $F_{vdW}$ , is given by [68,69]

$$F_{vdW} = \frac{A_{132} d}{12 h^2} \quad (1)$$

where  $d$  is the particle diameter and  $h$  is the separation distance between the particle and the substrate surface, usually taken to be 4 Å.[70]

The van der Waals-London force will increase if there is adhesion-induced deformation of the particle or substrate, producing an increase in the contact area. The modified van der Waals-London force in this case is [71]

$$F_{vdW} = \frac{A_{132} d}{12 h^2} \left( 1 + \frac{2a^2}{d h} \right) \quad (2)$$

where  $a$  is the contact radius between the deformed particle and the substrate surface. However, because of the high intrinsic hardness of both SiO<sub>2</sub> and Si, it is not expected that

either will suffer this deformation,[72] so that Eq. (1) applies.

$A_{132}$  is called the Hamaker constant and is given by

$$A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \quad (3)$$

where  $A_{11}$ ,  $A_{22}$ ,  $A_{33}$  are the Hamaker constants of the pure materials 1, 2 and 3. These pure material Hamaker constants vary from nearly zero for polymers to 3 eV for metals. The “binary” Hamaker constants,  $A_{12}$ ,  $A_{13}$  and  $A_{23}$ , are calculated using various mixing rules, the most common being a geometric mean:[73,74,75]

$$\begin{aligned} A_{12} &= A_{11}^{1/2} A_{22}^{1/2} \\ A_{13} &= A_{11}^{1/2} A_{33}^{1/2} \\ A_{23} &= A_{22}^{1/2} A_{33}^{1/2} \end{aligned} \quad (4)$$

Combining Eqs. (3) and (4), we have

$$A_{132} = \left( A_{33}^{1/2} A_{33}^{1/2} \right) + \left( A_{22}^{1/2} A_{11}^{1/2} \right) - \left( A_{33}^{1/2} A_{22}^{1/2} \right) - \left( A_{33}^{1/2} A_{11}^{1/2} \right) \quad (5)$$

or

$$A_{132} = \left( A_{11}^{1/2} - A_{33}^{1/2} \right) \left( A_{22}^{1/2} - A_{33}^{1/2} \right) \quad (6)$$

Various methods have been proposed to estimate the pure material Hamaker constants using experimentally accessible quantities. One such model,[76] applicable to non-polar (having no permanent dipole moment) molecules and



which therefore exhibit only the van der Waals-London force, relates  $A_{ii}$  to the work of cohesion:

$$A_{ii} = 24 \pi \gamma_i (d_0^2)_i \quad (7)$$

where  $\gamma_i$  is the surface tension and  $(d_0^2)_i$  is approximately equal to the molecular diameter of material i. Using  $\gamma_{\text{liquid CO}_2} \approx 0.6 \text{ dyne/cm}$  at  $25^\circ\text{C}$ , [77] and assuming  $d_0 = 0.20 \text{ nm}$ , [78]

$$A_{33} = A_{\text{liquid CO}_2} = 0.011 \text{ (eV)} \quad (8)$$

This approach cannot be used to calculate the Hamaker constant of SCCO<sub>2</sub> since, by definition, a supercritical fluid has no surface tension. The general expression for the Hamaker constant between molecules of material i is

$$A_{ii} = \pi^2 q^2 \beta_{ii} \quad (9)$$

where  $q$  is the number of atoms per unit volume (Loschmidt number),  $\beta_{ii}$  is given by [79]

$$\beta_{ii} = \left( \frac{3}{4} \alpha_0^2 \hbar \nu_0 \right), \quad (10)$$

$\hbar$  is Planck's constant ( $\hbar = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$ ),  $\nu_0$  is the ground-state frequency of the electron

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{e^2}{\alpha_0 m_e}}, \quad (11)$$

$e$  is the electron charge ( $e = 1.60 \times 10^{-19} \text{ C}$ ),  $m_e$  is the electron rest mass ( $m_e = 9.11 \times 10^{-31} \text{ kg}$ ), and  $\alpha_0$  is the molecular polarizability. For non-polar molecules like CO<sub>2</sub>, the polarizability can be found from the Clausius-Mossotti (C-M) function

$$C-M = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{\rho} = \frac{4}{3} \pi N_0 \alpha_0 \quad (12)$$

Where  $\epsilon$  is the dielectric constant,  $\rho$  is the density,  $M$  is the molecular weight and  $N_0$  is Avogadro's number. Michels and Kleerekoper [80] have shown, through measurements of  $\epsilon$  and  $\rho$ , that over a wide range of temperatures and pressures, including both liquid and supercritical CO<sub>2</sub>,  $\alpha_0 = (2.97-3.05) \times 10^{-30} \text{ m}^3$

Assuming  $\alpha_0 = 3.0 \times 10^{-30} \text{ m}^3$ , along with  $\rho_{\text{SCCO}_2} = 0.668 \text{ g/cm}^3$  at  $50^\circ\text{C}$  and 2000 psi (136 atmospheres), we have  $\nu_0 = 1.46 \times 10^{15} \text{ s}^{-1}$ ,

$$\beta_{11} = 8.71 \times 10^{-76} \text{ J}\cdot\text{m}^6, \text{ and}$$

$$A_{33} = A_{\text{SCCO}_2} = 0.045 \text{ (eV)} \quad (13)$$

For comparison, London [81] reports  $\alpha_0 = 2.86 \times 10^{-30} \text{ m}^3$  and

$\beta_{11} = 2.18 \times 10^{-77} \text{ J} \cdot \text{m}^6$  for gaseous  $\text{CO}_2$ .

For  $\text{SiO}_2$ , Si and water, the following Hamaker constants have been reported:  $A_{\text{SiO}_2} = 1.02 \text{ (eV)}$ , [82]  $A_{\text{Si}} = 1.6 \text{ (eV)}$ , [83] and  $A_{\text{H}_2\text{O}} = 0.27 \text{ (eV)}$ . [84] Substituting these values into Eq. (6), we have  $A_{132} = A_{\text{SiO}_2/\text{liq. CO}_2/\text{Si}} = 1.05 \text{ (eV)}$ ,  $A_{132} = A_{\text{SiO}_2/\text{SC CO}_2/\text{Si}} = 0.84 \text{ (eV)}$ , and  $A_{132} = A_{\text{SiO}_2/\text{H}_2\text{O}/\text{Si}} = 0.37 \text{ (eV)}$  For comparison, Menon *et al.* [85] gives  $A_{\text{glass}/\text{H}_2\text{O}/\text{Si}} = 0.07 \text{ (eV)}$ . Finally, Eq. (1) gives

$F_{\text{vdW}}^{\text{SiO}_2/\ell\text{-CO}_2/\text{Si}} \text{ (dynes)} = 8.762 \times 10^{-3} d$   
 $, F_{\text{vdW}}^{\text{SiO}_2/\text{SCCO}_2/\text{Si}} \text{ (dynes)} = 7.010 \times 10^{-3} d$   
 $, F_{\text{vdW}}^{\text{SiO}_2/\text{H}_2\text{O}/\text{Si}} \text{ (dynes)} = 3.088 \times 10^{-3} d$ ,  
 where  $d$  is in microns.

From Eq. (6), it can be seen that the Hamaker constant of the immersed, particle/fluid/surface system is lower than that of the unimmersed particle/substrate system, resulting in a decrease in the van der Waals-London force, due primarily to electrical screening. The reduction is greatest for immersion in water.

## B. Electrostatic Force

### 1. Electrostatic image force

When a charged, insulating particle such as  $\text{SiO}_2$  approaches an uncharged conductive surface such as (doped) Si, the requirement for overall charge neutrality generates an equal but oppositely charged “particle” within the Si, Figure 5. These oppositely charged “particles” act, essentially, as two plates of a capacitor, creating a net attractive force. This electrostatic image force,  $F_{\text{image}}$ , is often the predominate force for larger particles (greater than approximately 5 microns in diameter) [86] and is given by

$$F_{\text{image}} = \frac{Q^2}{4\pi\epsilon_0\epsilon l^2} \quad (14)$$

where  $Q$  is the charge on the particle,  $\epsilon$  is the permittivity of the immersion

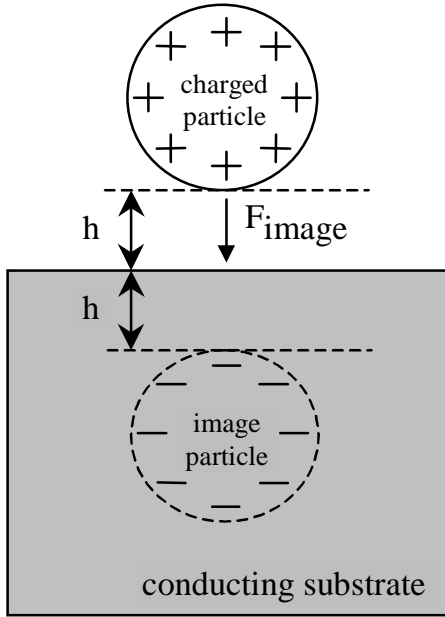


Figure 5. Image force generated by Coulomb attraction between a positively charged particle and its negatively charged “image” particle.

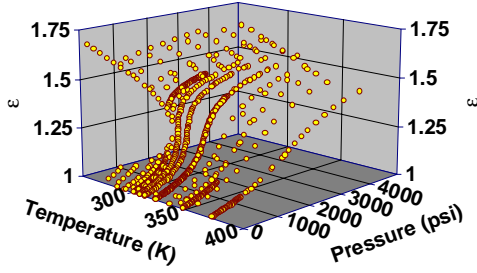


Figure 6. Experimentally measured values of the dielectric constant,  $\epsilon$ , of pure  $\text{CO}_2$  as a function of temperature and pressure.

medium between the particle and the surface,  $\epsilon_0$  is the permittivity of vacuum,

$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2/(\text{N}\cdot\text{m}^2)$ , and  $l$  is the separation distance between the charge centers (approximately equal to  $2r$  when the charge is uniformly distributed on the particle surface). If the charge density on the  $\text{SiO}_2$  particle is 10 electron charges per square micron,[87]

$$F_{\text{image}} \text{ (dynes)} = \frac{2.28 \times 10^{-8} d^2}{\epsilon} \quad (15)$$

where  $d$  is in microns.

Immersion of the particle/surface system in a fluid affects the magnitude of  $F_{\text{image}}$  through shielding of electrical charges, as manifested through the dielectric constant. The high static dielectric constant of water,  $\epsilon \approx 80$ , compared to  $\epsilon \approx 1.5$  for liquid  $\text{CO}_2$  (15°C and 800 psi), and  $\epsilon \approx 1.4$  for  $\text{SCCO}_2$ , (50°C and

2000 psi) (see Figure 6) results in higher image forces for immersion in  $\text{CO}_2$  for a given particle charge.

## 2. Electrical double layer force

When two dissimilar materials come into contact, a surface contact potential is created due to the difference in their respective work functions. The resulting surface charge buildup needed to preserve charge neutrality sets up a double-layer charge region, creating an electrostatic attraction. In dry environments, this electrical double layer force dominates for smaller particles, less than approximately 5 microns in diameter.[88] This electric double layer force,  $F_{\text{dbl}}$ , is given by

$$F_{\text{dbl}} = \frac{\pi \epsilon_0 d \phi^2}{2 h} \quad (16)$$

where  $\phi$  is the contact potential established on contact of the two materials and is equal to the numerical difference in their work functions.[89] Assuming  $\phi = 0.5 \text{ V}$  [90,91,92,93,94] and again using  $h = 4 \text{ \AA}$ ,

$$F_{\text{dbl}} \text{ (dynes)} = 8.69 \times 10^{-4} d \quad (17)$$

where  $d$  is in microns.

Immersion in a fluid will affect the magnitude of  $F_{\text{dbl layer}}$  through charge neutralization.[95] In practice, the initial contact potential will decrease with time because the high electrical conductivity of doped

Si will result in the charge “leaking away”.

### C. Capillary Force

If a surface-adhered particle is subjected an environment where there is a high vapor pressure of condensable fluid, the fluid may condense in the gaps between the particle and the substrate surface, Figure 7. The surface tension of this condensate draws the surfaces together, resulting in capillary attraction.[96] It is observed that the adhesion of particles to surfaces increases with relative humidity,[97] indicating that capillary force,  $F_{\text{cap}}$ , can make a significant contribution to overall adhesion. For high relative humidities ( $> 50\%$ ), for materials which are wetted by the fluid, and for materials having similar wetting properties,  $F_{\text{cap}}$  is given by [98,99]

$$F_{\text{cap}} = 2 \pi d \gamma \quad (18)$$

or

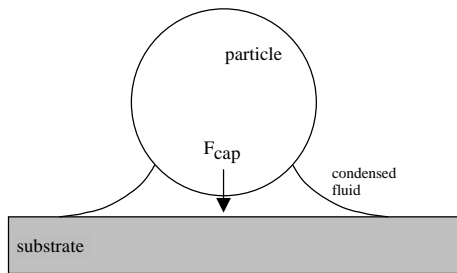


Figure 7. Schematic illustration of the meniscus formed by a condensable fluid and resulting capillary force.

$$F_{\text{cap}} \text{ (dynes)} = 6.28 \times 10^{-4} d \gamma \quad (19)$$

where  $d$  is in microns and  $\gamma$  is in dynes/cm.

If the particle/substrate system is totally immersed in a fluid which wets both materials, including liquid  $\text{CO}_2$  and water, the capillary force should be eliminated.[100] This is also true for  $\text{SCCO}_2$  because a supercritical fluid, by definition, cannot be made to condense.

### D. Gravitational Force

A solid particle will experience a downward gravitational force,  $F_{\text{grav}}$ , tending to hold it down onto a horizontal surface. (We assume that the particle is at its distance of closest approach to the substrate so that the buoyancy force can be neglected.)  $F_{\text{grav}}$  is given by

$$F_{\text{grav}} = \frac{\pi}{6} d^3 \rho g \quad (20)$$

For  $\text{SiO}_2$ ,  $\rho = 2.60 \text{ g/cm}^3$  and  $g = 980.67 \text{ cm/s}^2$ , so that

$$F_{\text{grav}} \text{ (dynes)} = 1.34 \times 10^{-9} d^3 \quad (21)$$

where  $d$  is in microns.

If the particle and the substrate surface are immersed, then the actual particle density,  $\rho$ , should be replaced by the apparent density,  $(\rho - \rho_{\text{fluid}})$ . However, the densities of liquid  $\text{CO}_2$ , supercritical  $\text{CO}_2$  and

water are similar, Figure 2, so that Eq. (21) will not be greatly changed.

Thus far, we have considered “static” forces acting between the SiO<sub>2</sub> particle and the Si surface. Typically, however, particulate removal is accomplished by immersion cleaning with a *flowing* solvent. This fluid motion generates two additional, hydrodynamic forces: lift and drag. In the following sections, the magnitudes of these forces will again be examined for liquid CO<sub>2</sub>, supercritical CO<sub>2</sub> and liquid water as the immersion media, for both laminar and turbulent flow conditions.

### E. Drag Force

O’Neill [101] gives an exact solution to the linearized Stokes flow equation for the case of a uniform linear shear flow, Figure 8, and for low values of the Reynolds number

$$F_{\text{drag}} = 1.7009 \times 3 \pi \eta d V_{y=r} \quad (22)$$

where  $V_{y=r}$  is the fluid velocity at a distance  $r$  normal to the substrate surface ( $r$  is the radius of the particle). For laminar flow, the velocity gradient is related to the fluid viscosity by

$$\tau_0 / \eta = \left( dV / dy \right)_{y=0} \quad (23)$$

where  $\tau_0$  is the shear stress on the substrate surface due to the flow.[102] Also, since the velocity gradient of the flow is linear, we can integrate Eq. (23) from  $y = 0$  to  $y = r$ , where  $V = 0$  at  $y = 0$ :

$$r \tau_0 = \eta V_{y=r} \quad (24)$$

Substituting into Eq. (22), and collecting terms,

$$F_{\text{drag}} = 8.02 d^2 \tau_0 \quad (25)$$

Chitanvis *et al.*[103] have carried out an analysis for the case of turbulent flow with a viscous sublayer, deriving an expression for the drag force as a function of the fluid (stream) velocity,  $V$ :

$$F_{\text{drag}} = 10.2 \pi \rho \left( \frac{f}{2} \right) V^2 r^2 \quad (26)$$

where  $f$  is Fanning’s friction factor,  $f \approx 0.04$ . Simplifying Eq. (26) gives

$$F_{\text{drag}} = 0.16 \rho V^2 d^2 \quad (27)$$

Comparing this drag force with the frictional force, which varies linearly with particle diameter, they further show that the removal of the smallest particles by rolling varies as  $V^{-4/3}$  while removal by sliding varies as  $V^{-2}$ .

$$r \tau_0 = \eta V_{y=r} \quad (30)$$

Combining Eqs. (28-30) gives [106]

$$F_{\text{lift}} = 1.615 \eta^{-1} \rho^{1/2} \tau_0^{3/2} d^3 \quad (31)$$

In turbulent flow, where the turbulent flow component normal to the substrate surface varies quadratically with distance from the surface, Cleaver and Yates [107] give the lift force as

$$F_{\text{lift}} = 0.076 \rho \left( \frac{\eta}{\rho} \right)^2 \left( \frac{d \rho U^*}{\eta} \right)^3 \quad (32)$$

Again using Eqs. (29) and (30), we have

$$F_{\text{lift}} = 0.076 \eta^{-1} \rho^{3/2} \tau_0 d^3 \quad (33)$$

### F. Lift Force

The (idealized) gradient in flow velocity illustrated in Figure 8 shows that the flow past a surface-adhered particle is a function of the distance normal to the surface. The lower flow velocity at the bottom of the particle relative to the velocity of flow at the top of the particle results in a lifting force, tending to dislodge the particle in the direction of the surface normal. This force is exactly analogous to the lift generated by airfoils. The magnitude of the lift force,  $F_{\text{lift}}$ , will depend on the nature of the near-surface flow, and expressions have been put forward for different flow conditions.

Saffman [104] gives the inertial lifting force in a linear shear flow as

$$F_{\text{lift}} = 6.46 r^2 \zeta^{1/2} \left( \frac{dV}{dy} \right)^{1/2} V_{y=r} \quad (28)$$

where  $v = \eta/\rho$ . This equation was derived for the case of a small spherical particle in an unbounded, linear shear flow in the absence of wall effects, but serves as an approximation to the problem of a particle in a shear flow along a rigid wall.[105] As before,

$$\left( \frac{dV}{dy} \right)_{y=0} = \frac{\tau_0}{\eta} \quad (29)$$

and

### 3.2. Surfactants-

Surfactants, in addition to lowering the surface tension of liquids, are used to assist in particle removal by modifying the surface

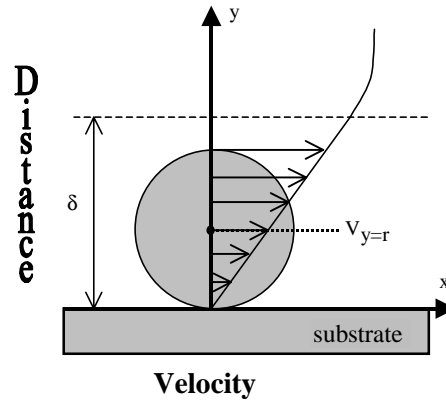
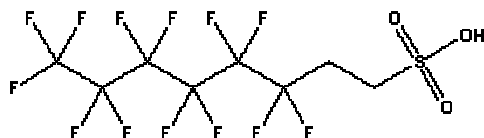
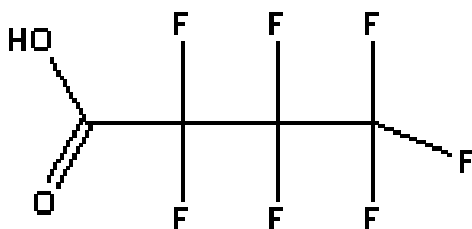


Figure 8. Schematic illustration of a linear shear flow past a surface-adhered particle.

charge/zeta potential of particle and/or substrate surfaces.[108] There are several compilations on the solubility of commercial surfactants in liquid and supercritical CO<sub>2</sub>. [109,110,111] These compilations show that there anionic, cationic and nonionic surfactants which have significant solubilities. Also, considerable progress has been made in the design of surfactants specifically for use in supercritical CO<sub>2</sub>, where it is well-known that highly fluorinated compounds exhibit excellent solubilities.[112,113] Figure 9 shows



1H,1H,2H,2H-  
Perfluorooctanesulfonic acid,  
miscible at  $P \approx 144$  bar and  
 $T = 50^\circ\text{C}$  [114]



perfluorobutyric acid, miscible at  
 $P \approx 186$  bar and  $T = 50^\circ\text{C}$  [115]

*Figure 9. Examples of surfactants which are completely miscible in supercritical CO<sub>2</sub>, along with the conditions where complete miscibility is observed.*

two representative examples of perfluorinated surfactants and the conditions of temperature and pressure where complete solubility in supercritical CO<sub>2</sub> is observed.

### 3. Discussion

The ability of CO<sub>2</sub>, particularly in the supercritical state, to remove organic contaminants would seem superior to the use of aqueous systems, which normally contain oxidizers along with acids or alkalies, since the former would be much less corrosive to fabricated surface structures.

The removal of trace metals using a sequence of acidic and/or alkaline aqueous rinses, i.e., SC-1 and SC-2, is capable of producing low levels of trace metals. Pure CO<sub>2</sub> does not solubilize these metals due to charge neutrality considerations, and would require the use of chelators. However, there are many such compounds which have been shown to be soluble and these would be required in very small amounts. Although any additive is undesirable in terms of potential residues, a final rinse using clean, dry CO<sub>2</sub> should remove these.

Inspection of Table 3 shows that, in general, adhesion forces between a particle and a surface vary linearly with the particle diameter. Removal forces, however, vary as a higher power of  $d$  (hydrodynamic drag acts on the cross-sectional area of the particle and therefore scale as

$d^2$ , while hydrodynamic lift, vibrational and centrifugal forces act on the volume of the particle and therefore scale as  $d^3$ ). Consequently, particle removal becomes more difficult as the particle size decreases.[116]

The calculations of the Hamaker constant for liquid and supercritical  $\text{CO}_2$  presented here are only approximate, but it is apparent that the resulting values of the van der Waals-London forces are higher than the corresponding value for immersion in water.

For the image force, it can be seen that the lower dielectric constant of both liquid and supercritical  $\text{CO}_2$  results in larger values of the image force, for a given particle charge.

Exact calculations for the lift and drag forces on a surface-adhered particle are extremely complex, and allow only trends to be deduced. However, the lift force depends inversely on fluid viscosity, which favors  $\text{CO}_2$ , Figure 10. For the drag force a higher viscosity is preferred, which is not favorable for  $\text{CO}_2$ . However, the boundary layer thickness, which is proportional to  $\sqrt{\frac{\eta}{\rho}}$ , would be much thinner. Also, the addition of soluble polymers might be used to independently adjust the viscosity of liquid and/or

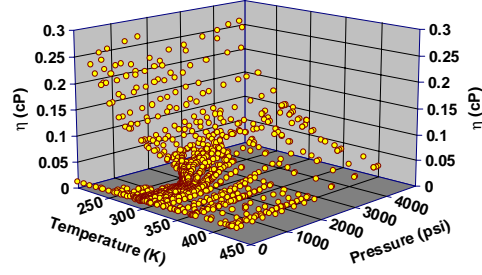


Figure 10. Empirically measured viscosity,  $\eta$ , in centipoise (cP) of pure  $\text{CO}_2$ , as a function of temperature and pressure.

supercritical  $\text{CO}_2$ .

It has been mentioned that the migration of surface-adhered particles due to Brownian motion and their subsequent agglomeration may be a mechanism by which the smallest particles are removed. This motion is greatly enhanced in both liquid and supercritical  $\text{CO}_2$  because of the low viscosity. The mean-square displacement,  $\bar{x}$ , by Brownian motion is given by

$$\bar{x} = \sqrt{\frac{2 k T t}{3 \pi \eta d}} \quad (34)$$

where  $T$  is the absolute temperature and  $t$  is time. The lower viscosity of liquid and supercritical  $\text{CO}_2$  (approximately a factor of 50 compared to water), along with the van der Waals attractive forces which exist between particles, would promote this agglomeration.[117]



Table 3. Effect on the various adhesion forces between a SiO<sub>2</sub> particle contacting a flat, horizontal Si surface immersed in (a) liquid CO<sub>2</sub>, and (b) supercritical CO<sub>2</sub> (SCCO<sub>2</sub>), and (c) H<sub>2</sub>O, based on the empirical relationships for these forces. All forces are given in dynes.

	SiO <sub>2</sub> / liq. CO <sub>2</sub> /Si	SiO <sub>2</sub> / SCCO <sub>2</sub> /Si	SiO <sub>2</sub> / water /Si
F <sub>vdW</sub>	$8.76 \times 10^{-3} d$	$7.01 \times 10^{-3} d$	$3.09 \times 10^{-3} d$
F <sub>dbl</sub>	$8.69 \times 10^{-4} d$	$8.69 \times 10^{-4} d$	$8.69 \times 10^{-4} d$
F <sub>image</sub>	$1.52 \times 10^{-8} d^2$	$1.62 \times 10^{-8} d^2$	$2.85 \times 10^{-10} d^2$
F <sub>cap</sub>	—	—	— $(6.28 \times 10^{-4} d \gamma)$
F <sub>drag</sub>	$8.02 d^2 \tau_0$	$8.02 d^2 \tau_0$	(laminar flow) $8.02 d^2 \tau_0$
	$\rho$ similar $\therefore$ similar F <sub>drag</sub>	$\rho$ similar $\therefore$ similar F <sub>drag</sub>	(turbulent flow) $0.16 \rho V^2 d^2$
F <sub>lift</sub>	lower $\eta \rightarrow$ $\rho$ similar $\therefore$ higher F <sub>lift</sub>	lower $\eta \rightarrow$ $\rho$ similar $\therefore$ higher F <sub>lift</sub>	(laminar flow) $1.615 \eta^{-1} \rho^{1/2} \tau_0^{3/2} d^3$
	lower $\eta \rightarrow$ $\rho$ similar $\therefore$ higher F <sub>lift</sub>	lower $\eta \rightarrow$ $\rho$ similar $\therefore$ higher F <sub>lift</sub>	(turbulent flow) $0.076 \eta^{-1} \rho^{3/2} \tau_0 d^3$
F <sub>grav</sub>	similar F <sub>grav</sub>	similar F <sub>grav</sub>	$1.34 \times 10^{-9} d^3$

Based on the foregoing analysis of adhesion forces for immersion in CO<sub>2</sub> versus water, it is probable that additional removal forces must be generated if dense-phase CO<sub>2</sub> is to achieve comparable removal forces obtainable with water-immersion. These forces can be generated in a number of ways, including increased shear flow, either through higher volumetric

flow rates or mechanical agitation of the wafer, or electrical forces.

We are currently performing experiments on pre-contaminated wafers to quantitatively evaluate the ability of dense-phase (liquid and supercritical) CO<sub>2</sub> to remove particulates, and the results of this study will be the subject of a future report.

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